

New Low-Temperature ZLD Process

WILLIAM A. SHAW, P.E., HPD, LLC, a Veolia Water Solutions & Technologies company, Pewaukee, WI

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ABSTRACT: ZLD systems can be very expensive from both a capital and operational perspective. New approaches to evaporator system design, especially low temperature evaporation, provide additional options to power plants which are looking for methods to effectively and economically reduce or eliminate their water discharges from FGD scrubbers and IGCC gasifiers.

INTRODUCTION

Conventional ZLD evaporation-crystallization processes for Flue Gas Desulfurization (FGD) scrubber blowdown and gasification waste streams have numerous drawbacks and shortcomings. These processes require clarification and extensive pretreatment of the wastewater with lime, soda ash and other chemicals to replace the calcium, magnesium, ammonium, and heavy metal ions in the wastewater with sodium ions so that a crystalline solid can be produced. Pre-treatment equipment and chemicals increase the footprint of the ZLD system as well as the capital costs and overall maintenance.

A new ZLD process is operated at low pressure. Lowering the operating pressure allows water from the waste stream to evaporate at lower temperatures. The chemistries of scrubber and gasifier wastewaters favor the formation of many hydrates and double salts which precipitate at lower concentrations as the temperature of the solution is lowered. The boiling point elevation of solutions is usually less at lower temperatures.

Upon concentration of the waste stream at

low temperature, dissolved solids will precipitate and crystallize at relatively low concentration. The low process temperature utilized eliminates the need to pre-treat the feed brine to the ZLD process. Elimination of the pretreatment avoids solids settling and filtration equipment, sludge dewatering equipment, and chemical feed/storage facilities, substantially reducing the footprint of the overall Wastewater Treatment Plant. It also avoids extensive sludge production with resulting costs for dewatering and landfill disposal. Low operating temperature reduces acid hydrolysis at high chloride concentration, allowing less noble alloys to be substituted for the high Ni-Cr-Mo alloy materials of construction usually required for a crystallizer train processing highly soluble chloride brines.

CURRENT TREATMENT METHODS

The burning or gasification of pulverized coal and petroleum coke in steam-electric power plants produces sulfur dioxide (SO₂) gas emissions, as well as HCl, HF, NO_x, fly ash, and many other chemical species. The 1990 Clean Air Act and its subsequent amendments mandated the reduction of power plant SO₂ emissions. The Best Available Technology for reducing SO₂

emissions is wet scrubber flue gas desulfurization (FGD) systems. These systems are designed to introduce an alkaline sorbent (usually limestone) in a water spray into the exhaust gas system of a coal-fired boiler. The alkali reacts with the SO_2 gas and other acid species and forms a slurry of predominately calcium sulfite. The calcium sulfite is oxidized to form gypsum, or calcium sulfate dihydrate, which is separated out for sale or disposal and most of the water is recycled. Similarly, a gas scrubbing step is utilized in most coal and petcoke gasification processes used in Integrated Gasification Combined Cycle (IGCC) power plants.

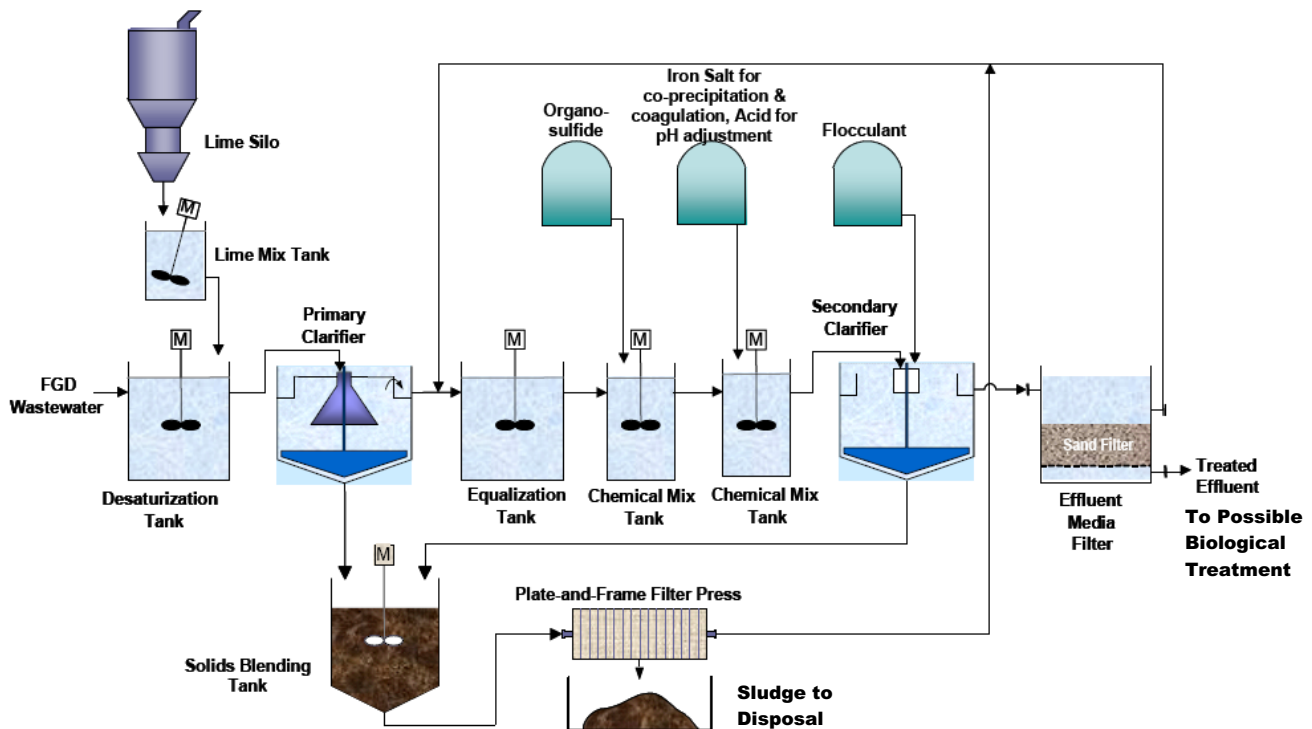
Wet scrubbers typically require a continuous blowdown to limit the accumulation of corrosive salts (particularly chlorides) and suspended solids absorbed from the gas stream. Although the composition of scrubber wastewaters varies widely, it is primarily a chloride purge stream with various cations and anions derived from the fuel (coal, petroleum coke, biomass, or a combination), the sorbent (limestone, lime, or ammonia), and the make-up water. Besides chloride, typical anions present include sulfate, fluoride, and salts of organic acids such as formate, acetate, and glycolate. There may also be a large concentration of nitrate depending on the conditions of combustion. The dominant cation in the wastewater depends on the sorbent used as the reagent in the scrubber – typically calcium if limestone or lime is used or ammonium if ammonia is used. Therefore, FGD and IGCC wastewaters are typically solutions of highly soluble salts such as calcium chloride or ammonium chloride, usually in the range of 30,000 to 60,000 mg/L. Discharge of these wastewaters is usually regulated due to the presence of

relatively small amounts of suspended solids and toxic contaminants such as heavy metals, selenium, boron, and organics. Some type of treatment is typically required to reduce or eliminate the suspended solids and toxins from the wastewater before it can be discharged to the environment.

PHYSICAL-CHEMICAL: The traditional treatment scheme to enable the liquid effluent from a wet limestone scrubber system to be discharged into a natural watercourse is a process in which the purge water from the scrubber is led into a series of reactor tanks where the gypsum in the purge stream is desaturated and heavy metals are precipitated by means of hydroxide/sulfide reaction by adding lime, organosulfide, and ferric chloride. Two precipitation/flocculation stages are usually included because of the wide variation in the optimum pH values for the precipitation of the metals present (Fig. 1). The presence of selenium, nitrates, and organics in the purge stream will probably require biological treatment prior to discharge. Such treatment methods can reduce the suspended solids, metals, acidity, and oxygen demand, but do not reduce the chloride or total dissolved solids. These chemical and biological treatment methods also produce sludges which increase several times the amount of solids to be disposed of.

When the sorbent is ammonia, and the wastewater is mainly ammonium chloride, the ammonia is often removed from the waste stream using a caustic stripper, replacing the dominant ammonium ions with sodium ions to produce a sodium chloride solution. This is done to avoid discharging ammonia, as it acts as a fertilizer in the environment.

Figure 1
Typical Physical-Chemical Treatment System for Chloride Purge Streams



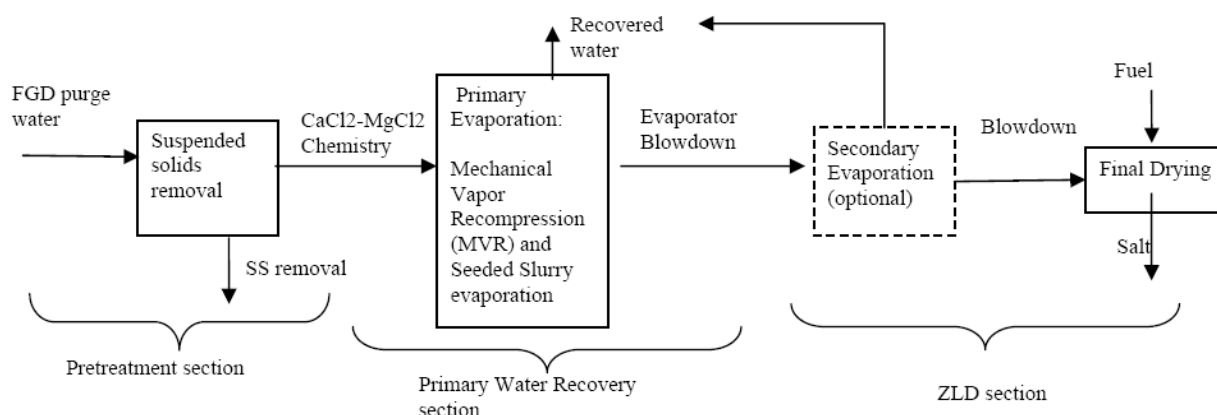
ZERO LIQUID DISCHARGE: As discharge limits become more stringent, physical, chemical, and biological treatment methods may not be able to reduce concentrations to the part per trillion levels required for discharge of some chemical species such as mercury and selenium. When conventional treatment methods are unable to treat high chloride purge streams to produce an effluent which meets the requirements of a discharge permit, evaporation of the purge stream has been utilized. The attractiveness of evaporation as a means to treat scrubber blowdown is that, in theory, all of the dissolved species, whether benign or hazardous or toxic, can be separated

completely from the water, producing a stable solid which can be landfilled and high quality distilled water for re-use in the plant. This results in zero discharge of wastewater to the environment.

In the present state of the art, two approaches have been used to achieve zero liquid discharge of high chloride purge streams from FGD scrubbers and IGCC gasifiers using evaporation.

Direct Evaporation: The first approach is diagrammed in Fig. 2 and involves three or four steps.

Figure 2
Evaporation of Wet Scrubber Purge Water – Process 1



The first step is clarification of the scrubber blowdown to reduce suspended solids to avoid plugging and flow problems in the following equipment and piping (Fig. 2). Chemicals such as ferric chloride and polymers are added to improve the settling of the suspended particles. The solids form a sludge which settles and is removed from the bottom of the clarifier.

The clarified feed flows to the evaporator feed tank (Fig. 3) where acid is added to neutralize alkalinity in the purge water so that the solution can be preheated in plate heat exchangers with minimal calcium carbonate scaling. Proprietary antiscalant formulations are usually added to avoid scaling in the preheaters due to other low solubility species present in the solution.

The preheated purge stream is then deaerated using steam from the evaporator to drive off dissolved carbon dioxide from the alkalinity reduction and any dissolved oxygen. This is done to minimize the potential for corrosion in the evaporator vessel. Most of the evaporation is done in a falling film evaporator seeded with calcium sulfate to minimize scale formation, and driven by a mechanical vapor compressor, (Fig. 3), where the boiling point elevation of the solution is low. To minimize the size and cost

of the vapor separator and compressor, evaporation is done at atmospheric pressure. Acid or caustic and antifoam may have to be added to the sump of the evaporator for pH and foam control.

The concentrated brine from the falling film evaporator may be sent to a surface impoundment (pond) for storage, or a forced circulation evaporator-crystallizer (Fig. 4) for further concentration. The forced circulation evaporator is driven by steam due to a high boiling point elevation of the solution. Calcium chloride and magnesium chloride have such high solubility in water that they do not crystallize out as normal salts do. Spray drying can be used to remove the remaining moisture from the concentrate and produce a dry product for disposal in a landfill. A spray dryer will require a fuel oil or natural gas supply, a baghouse to clean particulates from the air prior to exhaust to the atmosphere, and probably an air permit. Other methods of drying the evaporator concentrate are available. These include flakers, prilling towers, rotary dryers and other methods common to industrial salt production. The common drawback to drying technologies is that they are quite energy-intensive (as high as 1500 kWh per tonne of water removed) and the cost of fuel may thus be quite high to remove a fairly small quantity of water.

Figure 3
Chemical Addition, Preheating, Deaeration, and Primary Evaporation

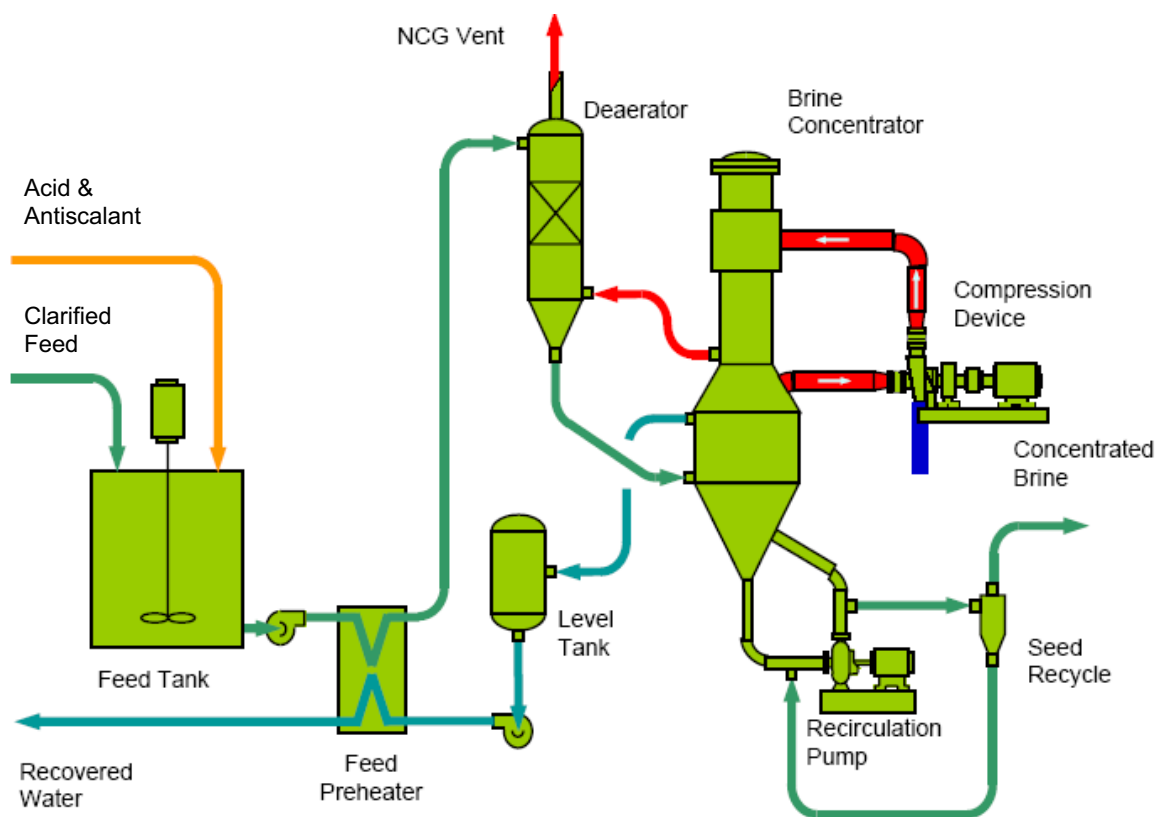
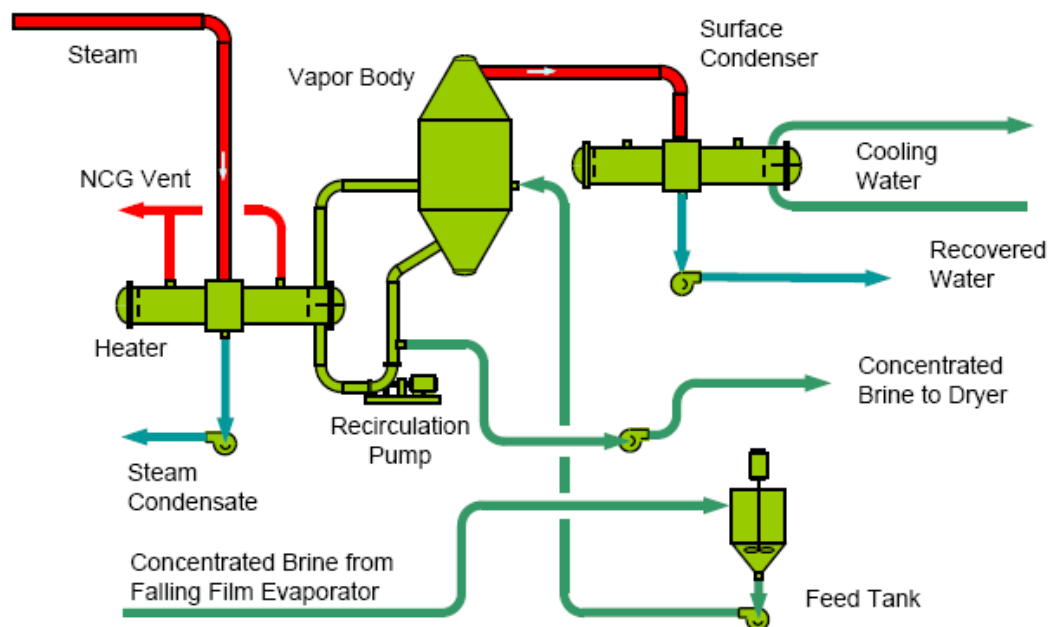


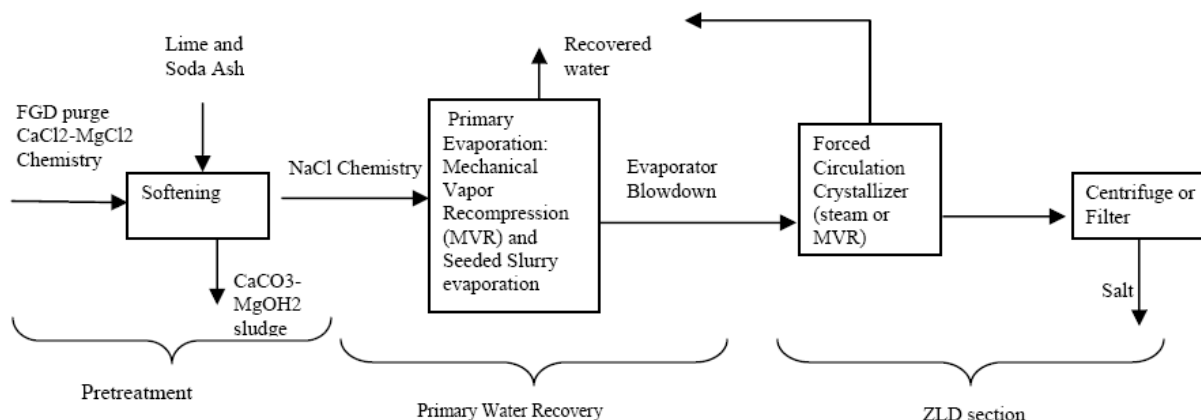
Figure 4
Further Concentration of Scrubber Purge in Steam-Driven Forced Circulation Evaporator



Pretreatment by Chemical Softening : The second approach (Fig. 5) used in wet limestone FGD purge evaporation systems involves chemical softening of the scrubber blowdown after a first clarification, prior to evaporation. Conventional lime-soda ash softening is used to remove most of the magnesium and calcium ions in the scrubber blowdown as precipitates of magnesium hydroxide and calcium carbonate. The net result of the softening process is that sodium ions are substituted for most of the calcium and magnesium ions and so the softened scrubber blowdown becomes mainly an aqueous solution of sodium chloride. The

softener sludge must be settled and dewatered and is disposed of in a landfill. The softened scrubber blowdown is then evaporated in a falling film evaporator seeded with calcium sulfate and driven by a mechanical vapor compressor, and water is recovered. The final concentration is done in a forced circulation evaporator-crystallizer, in which calcium sulfate and sodium chloride crystallize. A slurry of these salts in mother liquor is discharged from the evaporator into a centrifuge or pressure filter to further reduce the amount of water in the wet cake. This solid product is then disposed of in a landfill.

Figure 5
Evaporation of Wet Scrubber Purge Water – Process 2



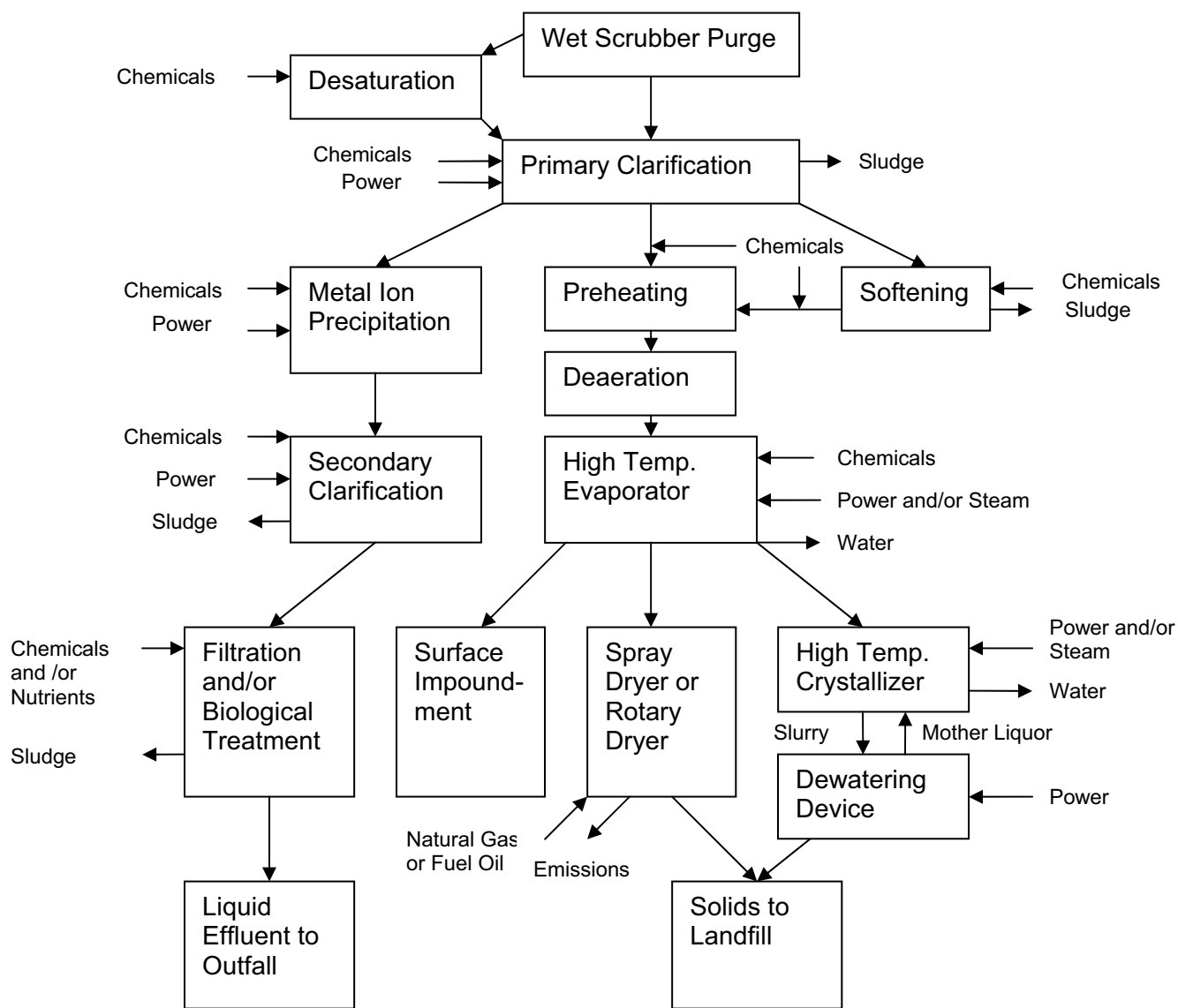
Evaporation of the softened purge water is done in a similar manner to Process 1 (Fig. 3). The softened purge water must be acidified to remove excess alkalinity, preheated, and deaerated. The falling film evaporator must be seeded to minimize scaling, as the purge water is saturated in calcium sulfate.

Since the softening step converts the chemistry of the purge water from a solution of calcium and magnesium chlorides to a solution of mainly sodium chloride, the concentrated brine from the falling film evaporator is sent to a forced circulation

evaporator-crystallizer (Fig. 4). Due to the limited solubility of sodium chloride, crystals of sodium chloride can be grown in the forced circulation unit. A slurry of crystals and mother liquor is withdrawn from the crystallizer and the crystals are dewatered in a centrifuge or pressure filter. The mother liquor is returned to the crystallizer for further concentration and the dewatered solids from the dewatering device are disposed of in a landfill.

Figure 6 presents a summary of the various treatment options available until now for FGD purge water.

Figure 6
Summary of Current Treatment Methods for Wet Scrubber Purge Water



NEW LOW TEMPERATURE CRYSTALLIZATION PROCESS

BACKGROUND: A unique low temperature crystallization process, known as the **CoLD** Process (**C**rystallization **o**f high solubility salts at **L**ow Temperature and **D**eeP Vacuum) has been developed. This crystallization process is derived from methods used in the industrial production of very soluble chloride salts. For example, crystallization of bischoffite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) at low temperature is done in the potash industry. Crystallization of carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$) is used in the same industry to recover KCl values from bitterns by concentration in evaporators at low temperature. Crystallization of hydrated salts of magnesium chloride and/or of tachyhydrite ($\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$) is done at low temperature in solar ponds.

The CoLD process is a very simple process, and is the only method which results in direct crystallization of highly soluble salts, including chlorides, nitrates, and salts of organic acids.

The CoLD process combines a conventional vacuum forced circulation crystallizer with conventional heat pump technology to take advantage of the reduced solubility and boiling point rise of high solubility salts at low temperature. Direct crystallization of calcium chloride, magnesium chloride, ammonium chloride, or other high solubility salts using the CoLD process eliminates the need for extensive pretreatment of the wastewater with lime, soda ash and other chemicals to replace the calcium, magnesium, and ammonium ions in the wastewater with sodium ions so that a crystalline solid can be produced. Elimination of the pretreatment avoids solids settling and filtration equipment, sludge dewatering equipment, and chemical feed/storage facilities, substantially reducing the footprint of the overall Wastewater Treatment Plant. It also avoids high chemical consumption and extensive sludge production with resulting costs for chemicals, dewatering, and landfill

disposal. The CoLD process produces a solid product consisting only of the solids originally contained in the wastewater plus a small amount of acid required to eliminate the bicarbonate alkalinity in the equalized wastewater.

The low operating temperature in the crystallizer reduces the requirements for high alloy materials of construction usually required for a crystallizer train processing high chloride brine. Direct crystallization of high solubility salts using the CoLD process also eliminates the need for inefficient and expensive drying equipment to produce a solid product for disposal.

OPERATING PRINCIPLE: For most wastewaters containing 1-5% dissolved solids by weight, it is relatively easy to remove 75-95 percent of the water in a falling film evaporator. When highly soluble salts are present in the wastewater, it is the last 5-25 percent of water that is difficult to evaporate.

As water is evaporated from a solution, the concentration and ionic strength of the salts increase as does the boiling temperature of the solution. The increase in boiling temperature of a solution above that of water at a given pressure is referred to as boiling point rise (BPR). The BPR increases as the concentration of dissolved salts increases when evaporating water from a solution.

Fig. 7 shows the boiling temperature for pure calcium chloride solution superimposed on its solubility curve at atmospheric pressure. One can see that as the concentration of calcium chloride increases, so does the boiling temperature. The two curves intersect at the solubility limit of calcium chloride in a boiling solution. Fig. 7 also shows that calcium chloride is very soluble in water; as a solution is concentrated by evaporation at 1 atm, its boiling point continues to rise, until the solubility limit of 75 wt% is reached. Fig.

Fig. 7 further shows that a saturated solution of calcium chloride at 1 atm has a BPR of 138°F (77°C) which results in a boiling temperature of almost 350°F (176°C). At this high temperature, calcium chloride, like magnesium chloride and ammonium chloride, undergoes hydrolysis in water; that is, it releases hydrochloric acid, which is very aggressive. The rate of hydrolysis increases with the temperature, so materials of construction for the evaporator vessels and heat transfer surface must be chosen carefully to resist the extremely corrosive nature of these salts at high concentrations and temperatures. Experience shows that suitable corrosion-resistant materials at these temperatures and concentrations are very expensive noble alloys, such as palladium-alloyed titanium and high nickel-chrome-molybdenum alloys. The requirement to use such expensive materials makes the use of a final crystallizer economically challenging in most wastewater ZLD applications.

A better option for dealing with highly soluble salts is to do the final crystallization at low temperature to take advantage of the fact that the solubility of highly soluble salts drops significantly with temperature.

Using the simplifying assumption that the phase diagram of pure calcium chloride solution (Fig. 7) is independent of pressure, we can see that several hydrated salts can form from calcium chloride solution, depending on the temperature. The concentration at which these hydrated salts form decreases with the temperature: e.g., calcium chloride dihydrate forms at 350°F (175.5°C) from a solution having a concentration of 75 percent CaCl_2 , but at 140°F (60°C) it will solidify from a solution having a concentration of only 58 percent by weight. By operating under vacuum, the boiling temperature of the solution is reduced from that at atmospheric pressure and a solid can be obtained at a relatively low concentration.

Fig. 8 shows that the boiling point rise is also lower when operating under vacuum at low temperature: at 75 percent CaCl_2 , the boiling point elevation is 75°C (135°F), but at 58 percent CaCl_2 , the boiling point elevation is only 33°C (59°F).

Figs. 8 and 9 demonstrate that a saturated solution of CaCl_2 (58% CaCl_2 by weight) will boil at 60°C (140°F) if the vapor pressure is maintained around 3.4 kPa (0.5 psia), well within the realm of typical industrial vacuum systems. The BPR of saturated CaCl_2 solution at these operating conditions is 33°C (59°F). This means that the water vapor which evaporates from the solution will be 33°C (59°F) less than the boiling temperature of the solution, or 27°C (81°F).

Usually, the FGD wastewater is derived from limestone scrubbing. Then, the solid precipitated in a low temperature CoLD crystallizer will be a mixture of mainly calcium sulfate and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). Should the scrubbing of the flue gas be based on the use of magnesia as the scrubbing reagent, magnesium sulfate and bischoffite, ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), would precipitate instead of calcium sulfate and calcium chloride dihydrate. If ammonia is used as scrubbing reagent, the resulting brine will contain ammonium sulfate and ammonium chloride.

Fig.10 depicts a schematic of a crystallizer designed to operate at the low temperature and pressure described above. In this system, the heat required to boil the solution and the cooling necessary to condense the water vapor are supplied by a closed cycle heat pump. The refrigerating fluid is heated by compressing it in the refrigerant compressor. Electrical energy, which drives the compressor motor, provides the work that is the source of heat for the crystallizer. Part of the heat imparted to the refrigerant by the compressor is transferred to the process solution in the crystallizer heat exchanger by the condensation of the refrigerant.

The liquid refrigerant flows through an expansion valve into the condenser, where it evaporates by heat transferred from condensing water vapor from the crystallizer. The cycle is closed as the refrigerant flows back to the compressor. The energy input is roughly 70 kWh per tonne of water evaporated.

Besides a lower boiling point elevation, the lower operating temperature results in a much lower acid hydrolysis rate for acid salts such as calcium chloride. The low temperature operation makes the selection of the materials of construction easier when dealing with mixtures of chloride salts, which are subject to hydrolysis. Low operating temperature translates to a much less aggressive solution and the material of construction need not be titanium or high Ni-Cr-Mo alloys. In fact, in the potash industry, carnallitic liquors are handled at low temperatures in carbon steel or rubber lined steel equipment.

Laboratory testing has proven the effectiveness of this process on typical wastewaters containing highly soluble salts. The solution depicted on the left in Fig. 11 is that of a typical wastewater from an FGD scrubber at a coal-fired power plant. After evaporation at low temperature (55°C,

131°F), the wastewater was separated into high quality distilled water and a stable solid on the right.

CONCLUSION

Environmental constraints are forcing more industries to evaluate the viability of ZLD treatment within their project scopes. The operational effectiveness and simplicity of evaporation at low temperature provide new opportunities to apply ZLD processes to more wastewater streams. Previous barriers to ZLD, such as high capital and operational expenses, can be mitigated using this process. The decreased metallurgical requirements and the lack of a major pretreatment facility such as a softening plant allow for lower capital costs. Additionally, low temperature evaporation does not require the use of pretreatment chemicals and greatly reduces the amount of sludge to be disposed.

The use of a heat pump eliminates the need for steam and greatly reduces the energy requirement to evaporate water. This results in significantly lower operational costs within a given facility. Evaporation at low temperature will allow industries with wastewaters containing highly soluble salts to achieve ZLD while maintaining or lowering capital and operating costs when compared to previous ZLD options.

Figure 7
Boiling Point and Solubility of Calcium Chloride at 1 atm

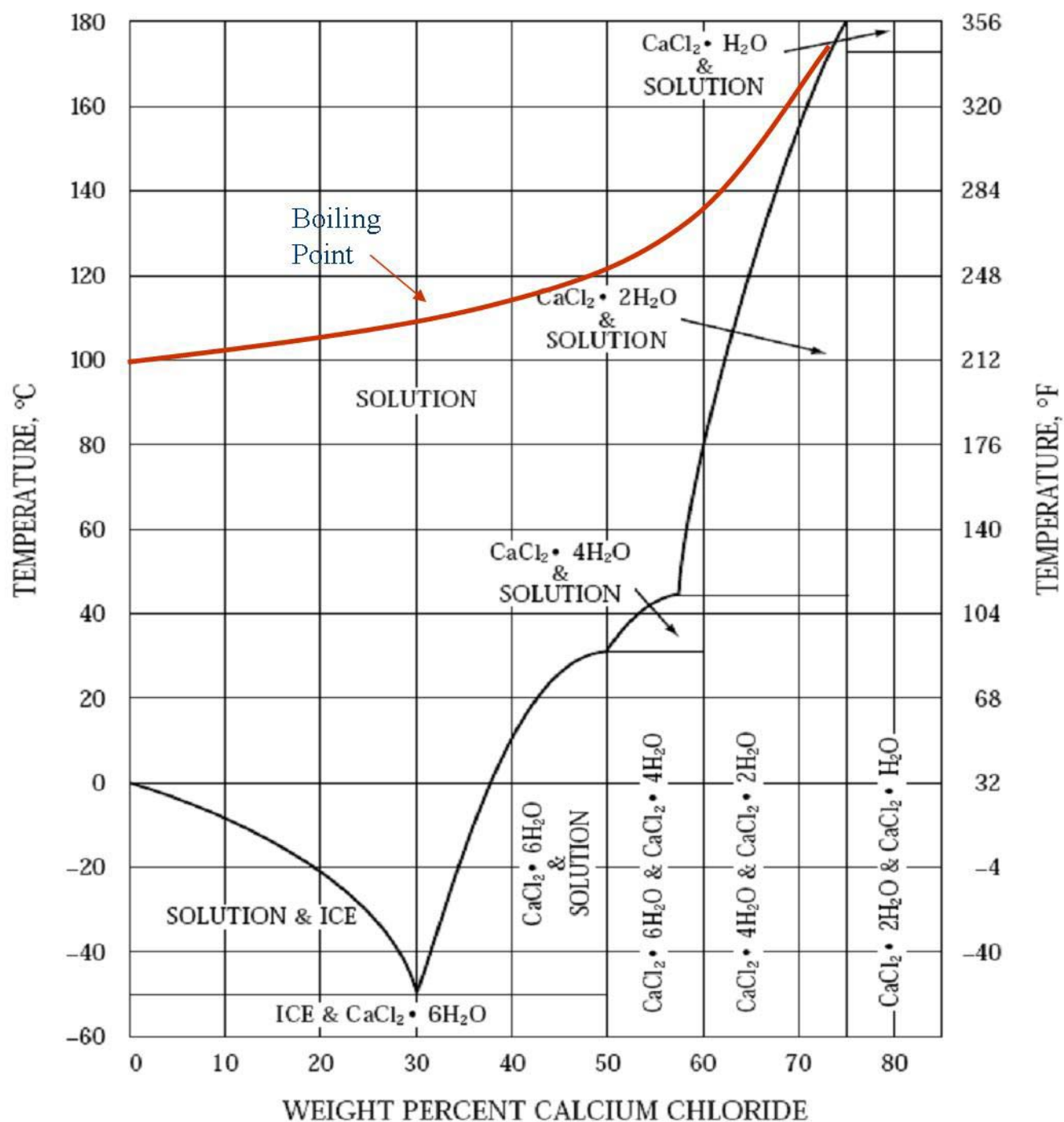


Figure 8

Boiling Temperature vs. Concentration, CaCl₂

Source: *International Critical Tables (1928), III, 368*

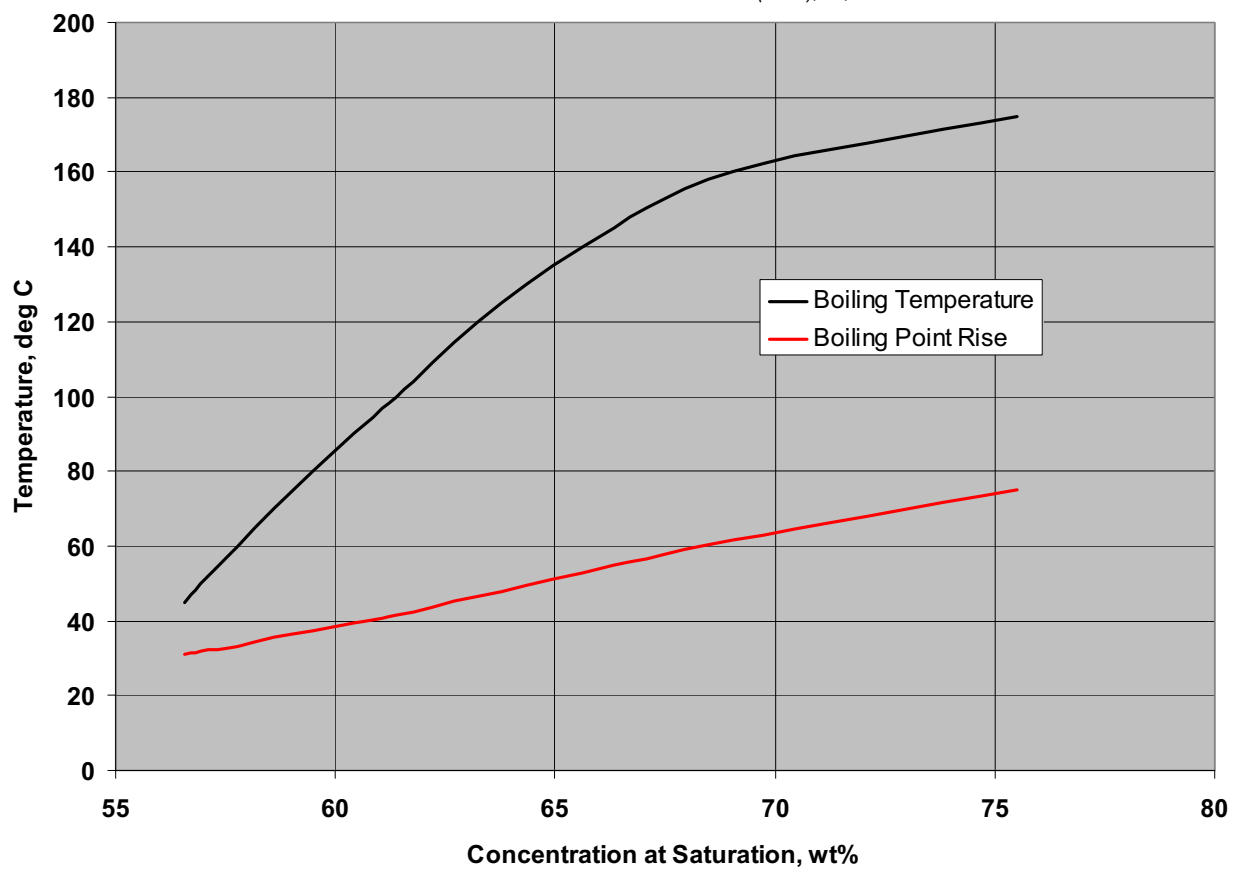


Figure 9
Boiling Temperature vs. Pressure, Saturated Solution of CaCl₂
Source: International Critical Tables (1928) III, 368

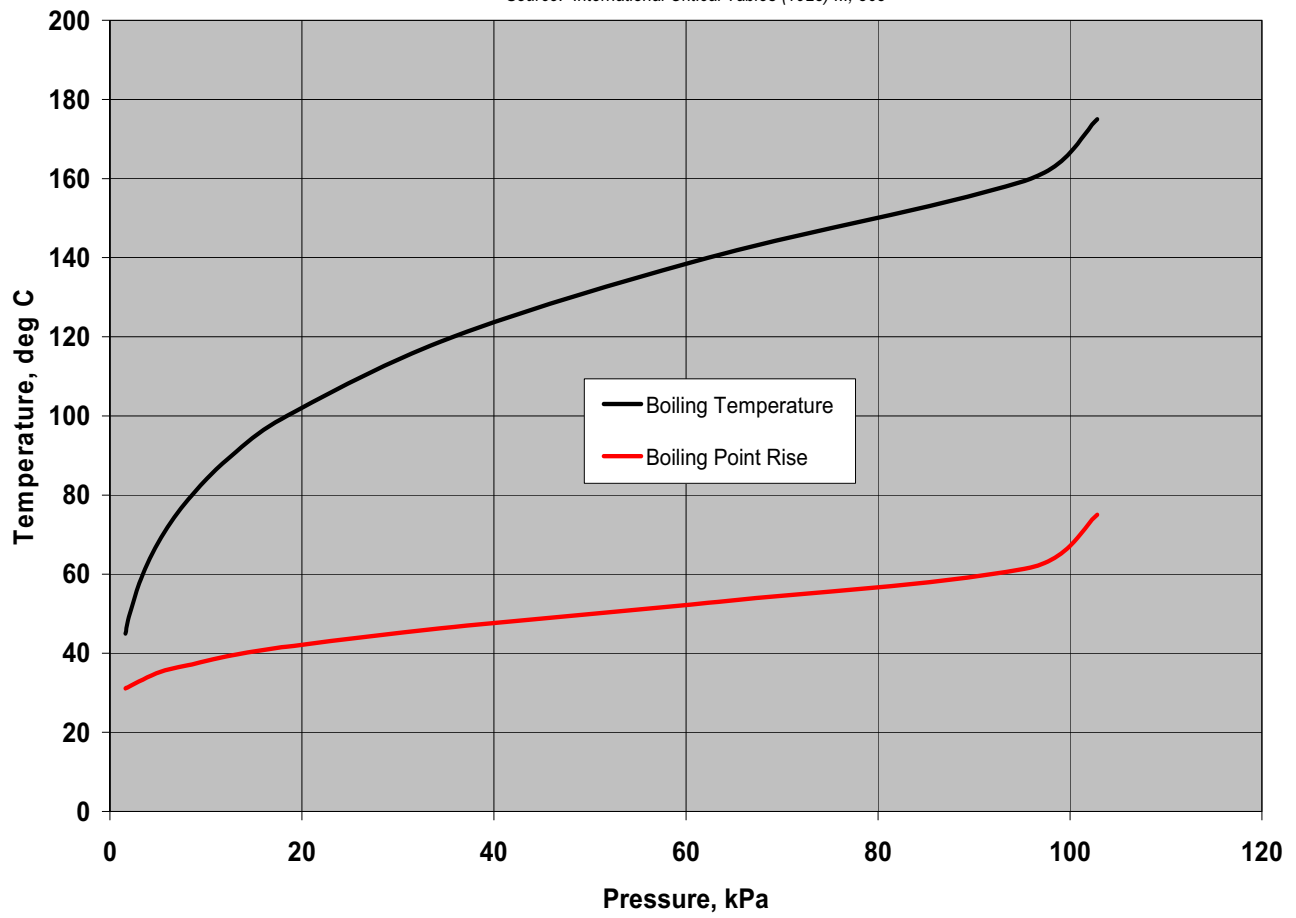


Figure 10
Low Temperature Heat Pump Crystallizer

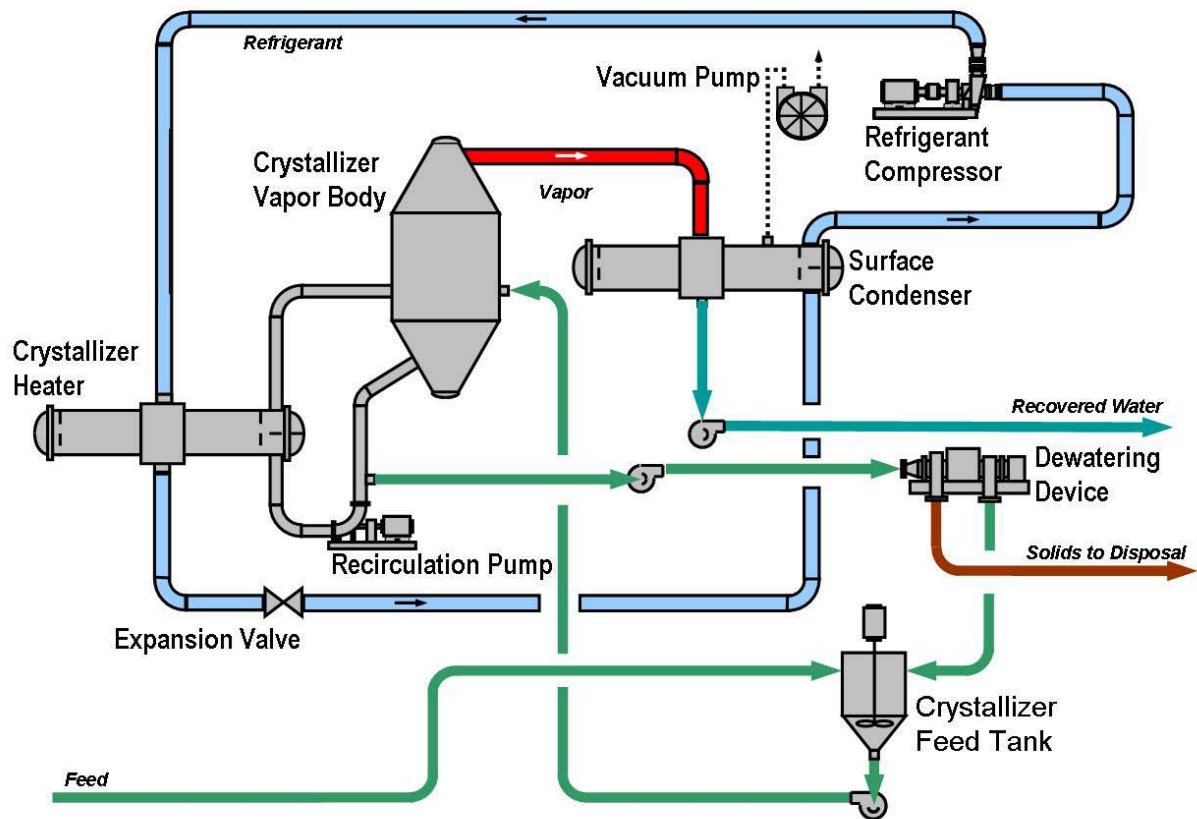


Figure 11
Results of Low Temperature Crystallization of FGD Scrubber Purge Water

